

PATENT ABSTRACTS OF JAPAN

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(54) CURABLE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject composition, improved in hard and brittle properties and weather resistance or the like while retaining the adhesion of an epoxy resin and useful especially as an elastic adhesive by including a specific vinylic monomer having a crosslinkable silyl group and an epoxy resin therein.

SOLUTION: This composition is obtained by mixing (A) a vinylic polymer, having at least one crosslinkable silyl group represented by the formula $[Si(R1)_2-b(Y)bO]_m-Si(R2)_3-a(Y)a$ [R1 and R2 are each a 1-20C alkyl, a 7-20C aryl or the like; Y is OH or the like; (a) is 0, 1, 2 or 3; (b) is 0, 1 or 2; (m) is an integer of 0-19, with the proviso that $[(a)+mb] \geq 1$] having preferably <1.8 ratio of the weight-average molecular weight to the number-average molecular weight, especially an acrylic or a methacrylic polymer with (B) an epoxy resin, especially a bisphenol A type epoxy resin at a mixing ratio of the components A/B within the range of (100/1) to (1/100) expressed in terms of weight ratio.

*NOTES *

JP0 and NP01 are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.*** shows the word which can not be translated.

3.In the drawings, any words are not translated.

CLAIMS

[Claim 1]

[Claim 1] The following two ingredients: A vinyl system polymer which has at least one crosslinkable silyl group shown by (D) general formula (1), a hardenability constituent which uses a (D) epoxy resin as an essential ingredient.



[Each of R¹ and R² denotes a formula An alkyl group of the carbon numbers 1-20, An aryl group of the carbon numbers 6-20, an aralkyl group of the carbon numbers 7-20, or (R³)₂SO - (R³) is a univalent hydrocarbon group of the carbon numbers 1-20, and three R³ being the same and differing - - - when the Tori ORGANO silox group shown is shown and R¹ or two or more R² exist, they may be the same and may differ. When Y shows a hydroxyl group or a hydrolytic basis and two or more Y exists, they may be the same and may differ, a shows 0, 1, 2, or 3, and b shows 0, 1, or 2, m is an integer of 0-19. However, it shall satisfy that it is $\text{armb} > 1$.]

[Claim 2] The hardenability constituent according to claim 1 whose ratio of weight average molecular weight and a number average molecular weight which were measured with gel permeation chromatography of a vinyl system polymer of an ingredient is less than 1.8.

[Claim 3] A vinyl system polymer of an ingredient is a hardenability constituent given in any 1

paragraph among claims 1-2 which are acrylic (meta) polymers.

[Claim 4] It is a hardenability constituent given in any 1 paragraph among claims 1-3, wherein a manufacturing method of a vinyl system polymer of an ingredient is a living-radical-polymerization method.

[Claim 5] It is a hardenability constituent given in any 1 paragraph among claims 1-4, wherein a manufacturing method of a vinyl system polymer of an ingredient is the atomic move RAJIPARU polymerizing method.

[Claim 6] It is a hardenability constituent given in any 1 paragraph among claims 1-5 which have the crosslinkable silyl groups shown by a general formula (1) of an ingredient in at least one molecular chain.

[Claim 7] A process (1) organic halogenated compound of the following [polymer / which has at least one crosslinkable silyl groups shown by a general formula (1) of an ingredient / vinyl system]. Or a vinyl system polymer which has halogen at the end and by using a sulfonil halide compound as an initiator and carrying out the radical polymerization of the vinyl system monomer by making a transition metal complex into a catalyst is manufactured. (2) By making a oxy anion which has an alkyl group react, and replacing halogen. It is a hardenability constituent given in any 1 paragraph among claims 1-6 which are the polymers obtained by, to which a hydrosilane compound which has the crosslinkable silyl groups which manufactures a vinyl system polymer which has an alkyl group at the end, and is shown by (3) general formulas (1) is made to react.

[Claim 8] By polymerizing by a living-radical-polymerization method, a vinyl system polymer which has the crosslinkable silyl groups shown by a general formula (1) of an ingredient the following process (1) vinyl system monomers. Manufacture a vinyl system polymer and a vinyl system polymer which has an alkyl group at the end and by making a compound which (2) Continues and has at least two alkyl groups of polymerization nature react is manufactured. It is a hardenability constituent given in any 1 paragraph among claims 1-6 which are the polymers obtained by, changed into a silyl group content substituent by making a hydrosilane compound which has the crosslinkable

alkyl groups which shows an end alkyl group by the general formula 1 react.

[Claim 9] An epoxy resin of an ingredient is a hardenability constituent given in any 1 paragraph among claims 1-8 which are epoxidized A type epoxy resins.

[Claim 10] Elastic adhesives using a hardenability constituent given in any 1 paragraph among claims 1-8.

[Translation done.]

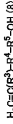
(R¹, R², a, b, and Y are the same as the above among a formula.)
Also in these hydroxylane compound, it is especially a general formula (7).
H-Si(R¹)₃-O⁻ M⁺ (7)

the compound which has a cross-linking group shown by (the inside of a formula, R², Y, and a are the same as the above) —, is desirable from an easy point.

[0032] When making the hydroxylane compound which has the above-mentioned crosslinkable silyl groups and an alkynyl group, a method is used in which the vinyl system polymer which has a carbon black, a platinum complex substance, aluminum silicate, and carbon black distribute a platinum solid as a transition metal catalyst. A complex with chloroplatinic acid, chloroplatinic acid, alcohol, aldehyde, ketone, etc., a platinum-olefin complex, and a platinum (0)-divinyl tetramethyl siloxane complex are mentioned. As an example of catalysts other than a platinum compound, RhO(Ph)₃, RhCl₃, RuCl₃, PdCl₂, FeCl₃, AlCl₃, PdCl₂·H₂O, NiCl₂·TiCl₄, etc. are mentioned.

[0033] (B) And the manufacturing method of the vinyl system polymer, which has at least one hydroxyl group used by the method of (A-2) - (A-7) is not limited to these methods, although the following methods are illustrated.

(B-a) A method to which the compound it has a compound, and the alkynyl group and hydroxyl group of polymerization nature in a monad which is mentioned, for example to the following general formula (8) when compounding a vinyl system polymer by a radical polymerization is made to react as the 2nd monomer.



(The inside of a formula, R³, R⁴, and R⁵ are the same as the above)

Although there is no restriction at the stage to which the compound it has a compound, and the alkynyl group and hydroxyl group of polymerization nature in a monad is made to react, it is especially living radical polymerization, and when it expects rubber character, it is preferred to make it react as the 2nd monomer after the bisphase of a polymerization reaction or the ending reaction of a predetermined monomer.

[0034] (B-b) A method to which 10-UNDESE Norborn 5-hexanol and alkynyl alcohol like silyl alcohol H-Si(R¹)₃-OH react after the bisphase of a polymerization reaction, or the ending reaction of a predetermined monomer for example when compounding a vinyl system polymer by living radical polymerization.

(B-c) For example, the method of carrying out the radical polymerization of the vinyl system monomer, using so much a hydroxyl group content chain transfer agent like the hydroxyl group content poly-sulfide shown in JP 5-262808A.

(B-d) For example, the method of carrying out the radical polymerization of the vinyl system monomer using hydrogen peroxide or a hydroxyl group content initiator as shown in JP 6-239912A and JP 8-283310A.

(B-e) For example, the method of carrying out the radical polymerization of the vinyl system monomer, using alcohols as shown in JP 6-118312A superficially.

(B-f) For example, the method of introducing a hydroxyl group into an end by making halogen of the vinyl system polymer which has a reactant high carbon-halogen bond in at least one piece react to hydrolysis or hydroxyl group-containing compound by a method as shown in JP 4-132709A etc.
(B-g) How to make the stabilization carbanion which has a hydroxyl group which is mentioned to a general formula (8) react to the vinyl system polymer which has at least one reactant high carbon-halogen bond (8) react to the vinyl system polymer which has at least one reactant high carbon-halogen bond, and to replace halogen by it.



(It is the same as the inside of a formula, and R², R³, R⁴ and sssss are)

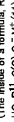
As an electron withdrawing group of R² and R³, especially the thing that has the structure of -CO₂R, -OCO R, and -ON is preferred.

[0035] (B-h) How to make the metal simple substance or organic metallic compound like zinc act on the vinyl system polymer which has at least one reactant high carbon-halogen bond for example, to prepare a eno anion, and to make aldehyde or ketone react to after an appropriate time.

(B-i) How to make the oxy anion or carboxylate anion which has a hydroxyl group as shown, for example in the general formula (10) or (11) react to the vinyl system polymer which has at least one reactant high carbon-halogen bond, and to replace halogen by it.



(The inside of a formula, R¹ and M⁺ are the same as the above)



(The inside of a formula, R¹ and M⁺ are the same as the above)

ss is mentioned.

[0036] When halogen does not participate in the method of introducing a hydroxyl group like (B-a) - (B-e) in this invention directly, it is preferred to compound a vinyl system polymer using a living-radical-polymerization method. The method of the point that control is easier to (B-b) is still more preferred. When introducing a hydroxyl group by changing halogen of the vinyl system polymer which has at least one reactant high carbon-halogen bond. Obtain by using an organic halogenated compound or a sulfonyl halide compound as an initiator, and carrying out the radical polymerization of the vinyl system monomer by making a transition metal complex into a catalyst (atom-transfer-radical-polymerization method). It is preferred to use for an end the vinyl system polymer which has at least one reactant high carbon-halogen bond. The method of of the point that control is easier to (B-i) is still more preferred.

[0037] A compound which has in a monad a basis which can react to crosslinkable silyl groups and a hydroxyl group like an isocyanate group. For example, gamma-isocyanato propyltrimethoxysilane, gamma-isocyanato propylmethyl dimethoxysilane, gamma-isocyanato propyl triethoxysilane, etc. are mentioned, and the catalyst of a urethane-ized reaction generally known as occasion demands can be mentioned.

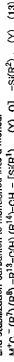
[0038] A compound it has a compound, and the alkynyl group and crosslinkable silyl groups of polymerization nature in the monad used by the method of (C). For example, what is shown with following general formula (12), such as trimethoxypolysiloxane (meta) acrylate and methyl dimethoxy silyl group (meta) acrylate, is mentioned.



(R¹, R², R³, R⁴, R⁵, Y, a, b, and m are the same as the above among a formula.) R⁷ may include one or more other bonds by the divalent organic group of direct coupling or the carbon numbers 1-20.

Especially although there is no restriction in particular at the stage to which the compound it has a compound, and the alkynyl group and crosslinkable silyl groups of polymerization nature in a monad is made to react, it is living radical polymerization. When it expects rubber character, it is preferred to make it react as the 2nd monomer after the bisphase of a polymerization reaction or the ending reaction of a predetermined monomer. The hydroxylate etc. which have the mercaptan which has crosslinkable silyl groups and crosslinkable silyl groups are shown in JP 2-146818B and JP 4-554413A which have crosslinkable silyl groups as mentioned.

[0039] The vinyl system polymer which is used by the method of (E) and which has at least one reactant high carbon-halogen bond can be obtained by the method of (E-a) - (E-b) as above-mentioned. What is shown by a general formula (13) as a compound having crosslinkable silyl groups and stabilization carbanion is mentioned into a monad.



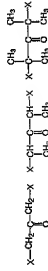
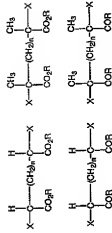
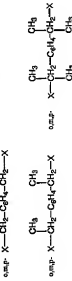
(It is the same as R¹, R², R³, R⁴, R⁵, Y, a, b, m, and sssss among a formula.) R⁷ may include one or more other bonds by the divalent organic group of direct coupling or the carbon numbers 1-10 shows hydrogen or the alkyl group of the carbon numbers 1-10, the aryl group of the carbon numbers 6-10, or the aralkyl group of the carbon numbers 7-10.

As an electron withdrawing group of R² and R³, especially the thing that has the structure of -CO₂R, -OCO R, and -ON is preferred.

[0040] The vinyl system polymer which crosslinkable silyl groups has at the end of an at least one-piece chain. In order to obtain an organic halogenated compound or a sulfonyl halide compound by the polymerizing method using an initiator and a transition metal complex as a catalyst, it is preferred to

use as an inhibitor the organic halogenated compound which has two or more resistant high carbon-halogen bonds used as the starting point, or a sulfonyl halide compound. As these examples, [0041]

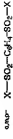
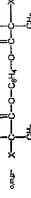
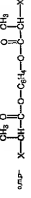
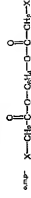
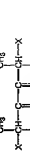
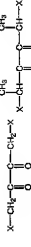
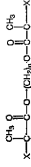
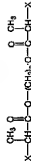
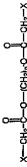
Formula 1]



[0042] (R expresses an alkyl group of the carbon numbers 1-20, the carbon number 6 - 20 aryl groups or the carbon number 7 - 20 aralkyl groups among a formula.) C_6H_4 expresses a phenylene group, n expresses an integer of 0-20, X expresses chlorine, bromine, or iodine.

[0043]

[Formula 2]



[0044] (X expresses chlorine, bromine, or iodine among a formula.) n expresses the integer of 0-20, C_6H_4 expresses a phenylene group, etc. — It is raised. Besides the above, the vinyl system polymer which has crosslinkable silyl groups at the end of an at least one-piece chain can be obtained. [0045] The organic halogenated compound which has crosslinkable silyl groups can be used as an initiator. The vinyl system polymer which has crosslinkable silyl groups at one end and which other ends have the structure of the general formula (1) will be obtained. Thus, if halogen of the alkyl end of the polymer obtained is changed into crosslinkable silyl groups, the polymer obtained will be a polymer which has crosslinkable silyl groups at both ends can be obtained. The already indicated method can be used as the converting method.

[0046] Although there is no restriction in particular as an organic halogenated compound which has crosslinkable silyl groups, what has the structure shown, for example in the general formula (14) and (15) is illustrated.



(R¹, R², a, b, m, X, and Y are the same as the above among a formula.) Independently R¹⁵ and R¹⁶ Hydrogen or an alkyl group of the carbon numbers 1-20. An aryl group of the carbon numbers 6-20, an aralkyl group of the carbon numbers 7-20 or a thing mutually connected in the other end, and R¹⁷ show -COO-, -O-, -O-, or -m-, m- and p-phenylene group. R¹⁸ in which R¹⁸ may include one or more other bonds by a divalent organic group of direct coupling or the carbon numbers 1-10 shows hydrogen or an alkyl group of the carbon numbers 1-10, an aryl group of the carbon numbers 6-10, or

(Comparative examples 3 and 4) The polymer obtained in the examples 1 and 2 of comparison composition instead of the polymer obtained in the synthetic example 1 was used, and also physical properties were measured like Example 2. The result was doubled and it was shown in Table 2.

[0065]

[Table 2]

例1+重合体	比較例2	比較例3	比較例4
合成例1	比較合成例1	比較合成例1	比較合成例2
M30(MPa)	4.9	1.5	0.4
せん断強度(MPa)	5.5	4.6	6.6

[0066] The shear strength of Example 2 is also high at a high modulus. The combination mixture of the comparative example 3 is hyperviscosity, and it is harder to deal with it than the thing of Example 2. The hardened materials were physical properties with them. [a modulus, the low shear strength, or] [insufficient as adhesives] Although the shear strength is enough, since the modulus is low, the deformation in joining becomes large too much, and it is unsuitable. [of the comparative example 4]

(Example 3) Epicoat 828 to vinyl system polymer 100 weight section obtained in the synthetic example 1 100 weight sections. The amount part of allend condensation catalyst (#918, product made from Sanhjo organicity) duplex, and 2,4,6-tris(dimethyl aminomethyl) phenol Ten weight sections. The amount part of N-(beta-aminoethyl)-gamma-aminopropyl trimethoxysilane duplex and water 1 weight section were mixed. It applied to the aluminum specimen of A1050P, and it was recuperated at 50 °± with the room temperature on the 4th on the 3rd. The hauling shear bending strength examination was done based on JIS K8850. The result was shown in Table 3.

(Comparative examples 5 and 6) The polymer obtained in the examples 1 and 2 of comparison composition instead of the polymer obtained in the synthetic example 1 was used, and also physical properties were measured like Example 3. The result was doubled and it was shown in Table 3.

[0067]

[Table 3]

例1+重合体	比較例5	比較例6
合成例1	比較合成例1	比較合成例2
せん断強度(MPa)	8.0	5.0 6.9

[0068] The combination mixture of the comparative example 5 is hyperviscosity, and it is harder to deal with it than the thing of Example 3. Example 3 and the comparative example 6 had sufficient intensity. However, since the comparative example 6 is a presentation which is not dissolved as the comparative example 2 showed, it is unsuitable from the point of the stable manifestation of physical properties. The intensity of the comparative example 5 is insufficient.

[Translation done.]